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MANUFACTURING METHOD FOR 2-HALOACRYLIC ACID AND DERIVATIVES THEREOF
[2-Haroakurirusan oyobi sono yuudoutai no seizou houhou]

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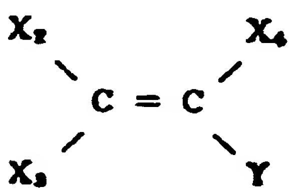
SPECIFICATION /219*

1. Title of the Invention

MANUFACTURING METHOD FOR 2-HALOACRYLIC ACID AND DERIVATIVES THEREOF

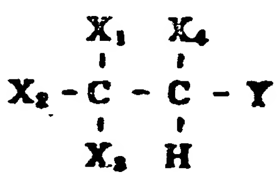
2. Claims

(1) Manufacturing method for 2-haloacrylic acid and derivatives thereof expressed by the general formula (II)



.... (II)

(wherein X_2, X_3, X_4, and Y are the same as those in the general formula (I) below) characterized by dehydrohalogenating a propionic acid derivative expressed by the general formula (I)



.... (I)

(wherein X_1 and X_4 are halogen atoms, X_2 and X_3 are a hydrogen atom or halogen atom, and Y is a carboxylic group, alkoxycarbonyl group, aryloxycarbonyl group, carbamoyl group, or cyano group) in the presence of a weakly basic ion exchange resin.

(2) A method of Claim (1) in which X_1 and X_4 are chlorine atoms and in which X_2 and X_3 are a hydrogen atom, chlorine atom, or bromine atom in general formula (I).

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* Numbers in the margin indicate pagination of the foreign text.

(3) A method of Claim (1) or Claim (2) in which X_2 and X_3 are hydrogen atoms in general formula (I).

(4) A method of Claim (1), (2), or (3) in which Y is a carboxylic group, alkoxycarbonyl group, or aryloxycarbonyl group in general formula (I).

(5) A method of Claim (1), (2), (3), or (4) in which the amount of the basic ion exchange resin is within a base-equivalent range of 1.0 ~ 10.0 per 1 mol of the propionic acid derivative expressed by general formula (I).

(6) A method of Claim (1), (2), (3), or (4) in which the amount of the basic ion exchange resin is within a base-equivalent range of 1.0 ~ 2.0 per 1 mol of the propionic acid derivative expressed by general formula (I). /220

(7) A method of Claim (1), (2), (3), (4), (5), or (6) in which the reaction is made to occur between approximately 0°C ~ 80°C.

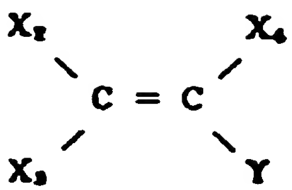
(8) A method of Claim (1), (2), (3), (4), (5), or (6) in which the reaction is made to occur between approximately 0°C ~ 60°C.

(9) A method of Claim (1), (2), (3), (4), (5), (6), (7), or (8) in which the reaction is made to occur in the presence of a solvent.

3. Detailed Explanation of the Invention

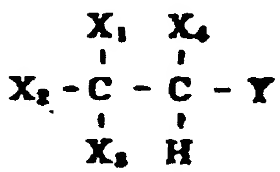
<Field of Industrial Application>

The present invention pertains to manufacturing methods for 2-haloacrylic acid and derivatives thereof, more specifically to manufacturing methods for 2-haloacrylic acid and derivatives thereof expressed by the general formula (II)



.... (II)

(wherein X_2, X_3, X_4, and Y are the same as those in the general formula (I) below) characterized by dehydrohalogenating a propionic acid derivative expressed by the general formula (I)



.... (I)

(wherein X_1 and X_4 are halogen atoms, X_2 and X_3 are a hydrogen atom or halogen atom, and Y is a carboxylic group, alkoxycarbonyl group, aryloxycarbonyl group, carbamoyl group, or cyano group) in the presence of a basic ion exchange resin, specifically a weakly basic ion exchange resin.

2-haloacrylic acid and derivatives thereof expressed by the general formula (II) and manufactured by the method of the present invention are important compounds used as raw materials for agricultural chemicals and medicines and as raw materials for functional polymer compounds such as UV or electron-beam photosensitive resists.

<Related Art>

It has been suggested in the past to manufacture 2-haloacrylic acid and its derivatives by dehydrohalogenating 2,3-dihalopropionic acid or its derivatives by means of a base such as sodium acetate (U.S. Patent No.2434229), sodium carbonate (U.S. Patent No.2245547), sodium hydroxide

(West Germany Unexamined Patent No.2350120), quinoline (J.Am.Chem.Soc., 623495(1940)), etc. or by means of a strong acid such as sulfuric acid (U.S. Patent No.2870193) or a sulfonic-acid-type ion exchange resin (U.S. Patent No.2862960).

<Problems that the Invention is to Solve>

However, in the manufacture of 2-haloacrylic acid and its derivatives in which said conventional techniques are utilized, the use of the aqueous solution of alkali metal salt such as sodium acetate or sodium carbonate as a dehydrohalogenating agent lowers the conversion ratio or generates the need to greatly extend the reaction time. On the other hand, when the aqueous solution of a strong alkali substance such as sodium hydroxide or potassium hydroxide is used as a dehydrohalogenating agent, side reactions such as hydrolysis or saponification become likely to occur, lowering the yield. Moreover, organic bases such as quinoline and N,N-dimethylaniline are expensive and it is troublesome to remove the generated hylogenated hydrogen salt from the reaction system. Moreover, large losses occur during recovery and reusing. When dehydrohalogenation is performed by using sulfuric acid or a sulfonic-acid-type ion exchange resin, the generated 2-haloacrylic acid and its derivatives are likely to polymerize.

In this manner, the shortcomings of these conventional techniques have been large obstacles in their implementations.

<Means for Solving the Problems>

In order to solve these problems, the present inventors diligently studied the manufacturing methods for 2-haloacrylic acid and its

derivatives. As a result, they discovered the fact that the 2-haloacrylic acid and its derivatives expressed by the general formula (II) can be obtained at high yields by dehydrohalogenating the propionic acid /221 derivative expressed by the general formula (I) by using a basic ion exchange resin, specifically a weakly basic ion exchange resin, and the present invention was thus completed.

The present invention is a manufacturing method for the 2-haloacrylic acid and its derivatives expressed by the general formula (II), and it is characterized by the propionic acid derivative expressed by the general formula (I) being dehydrohalogenated by means of a basic ion exchange resin, preferably a weakly basic ion exchange resin.

The use of a basic ion exchange resin has excellent effects in that it not only simplifies the removal of salt from a dehydrohalogenating agent but also allows the agent to be reused.

<Operation of the Invention>

Concrete examples of a propionic acid derivative expressed by the general formula (I) utilized in the present invention are: halogenated propionic acids such as 2,3-dichloropropionic acid, 2,3,3-trichloropropionic acid, 2,3,3,3-tetrachloropropionic acid, 2,3-dibromopropionic acid, 2,3,3-tribromopropionic acid, etc.; halogenated propionic esters such as methyl 2,3-dichloropropionate, ethyl 2,3-dichloropropionate, n-propyl 2,3-dichloropropionate, iso-propyl 2,3-dichloropropionate, n-butyl 2,3-dichloropropionate, iso-butyl 2,3-dichloropropionate, sec-butyl 2,3-dichloropropionate, tert-butyl 2,3-dichloropropionate, n-pentyl 2,3-dichloropropionate, n-hexyl

2,3-dichloropropionate, cyclohexyl 2,3-dichloropropionate, 2-ethylhexyl 2,3-dichloropropionate, n-octyl 2,3-dichloropropionate, iso-octyl 2,3-dichloropropionate, phenyl 2,3-dichloropropionate, pentachlorophenyl 2,3-dichloropropionate, 2,2,2-trifluoroethyl 2,3-dichloropropionate, 2,2,3,3,3-pentafluoro-n-propyl 2,3-dichloropropionate, methyl 2,3-dibromopropionate, ethyl 2,3-dibromopropionate, n-butyl 2,3-dibromopropionate, ethylhexyl 2,3-dibromopropionate, phenyl 2,3-dibromopropionate, and 2,2,2-trifluoroethyl 2,3-dibromopropionate; halogenated propionitrile such as 2,3-dichloropropionitrile, 2,3,3-trichloropropionitrile, 2,3,3-trichloropropionitrile, 2,3,3,3-tetrachloropropionitrile, 2,3-dibromopropionitrile, and 2,3,3-tribromopropionitrile; 2,3-dichloropropionamide; 2,3,3-trichloropropionamide; 2,3,3,3-tetrachloropropionamide; 2,3-dibromopropionamide; and 2,3,3-tribromopropionamide.

The dehydrohalogenation of the present invention advances even without the use of a solvent, but the use of a solvent is desirable in terms of reaction heat removal and resin washing and recovering. Examples of the solvent are alcohols such as water, methanol, ethanol, isopropanol, etc., ketones such as acetone, methylethylketone, etc., and nitriles, such as acetonitrile, etc., but preferred solvents are water, methanol, and acetone.

The dehydrohalogenation of the present invention advances favorably at a reaction temperature of 0 ~ 80°C, preferably 0 ~ 60°C. Outside the above temperature range, the reaction speed becomes slow, the volume of

the bases decreases due to the detachment the ion exchange resin's exchange groups, and the produced 2-haloacrylic acid and its derivatives become likely to polymerize.

A reaction in which a propionic acid derivative expressed by the general formula (I) is dehydrohalogenated by means of a basic ionic exchange resin is an excellent manufacturing method that allows the reaction to advance sufficiently at room temperature and with which 2-haloacrylic acid and its derivatives expressed by the general formula (II) can be quantitatively obtained.

A weakly basic ion exchange resin is preferred as the basic ion exchange resin utilized for the present invention, and examples of the ion exchange groups are those that have tertiary amines or pyridyl groups. A moderately basic ion exchange group resin or a strongly basic /222 ion exchange resin has a small volume of bases or a low dehydrohalogenation activity and does not provide the desired technical standards. An example of a weakly basic ion exchange resin containing tertiary amine as exchange groups is one that has a styrene-divinylbenzene copolymer as the base. Examples of a weakly basic ion exchange resin containing pyridyl groups as exchange groups are 2-vinylpyridine, 4-vinylpyridine homopolymers, and polyvinylpyridine resins such as copolymers of vinylpyridines and styrene or divinylbenzene.

The amount of resin used for the dehydrohalogenation of the present invention can be selected from the base-equivalent range of 1.0 ~ 10.0, preferably the base-equivalent range of 1.0 ~ 2.0, per 1 mol of the propionic acid derivative expressed by the general formula (I). If the

amount is smaller than the lower limit of the above range, the yield will decrease, and if the amount is larger than the upper limit of the above range, separation and recovering operations become troublesome, only causing economic disadvantages.

Moreover, the salt of a weakly basic ion exchange resin produced in the dehydrohalogenation can be easily separated by means of filtering and the salt can be reused easily by treating it with an aqueous solution of sodium hydroxide, potassium hydroxide, ammonia, etc. or with a methanol solution, acetone solutions, etc. and can be reused several tens of times in the same manner.

The present invention will be explained concretely based on working examples, but needless to say, the present invention is not limited to these working examples.

Working Example 1

500ml of a weakly basic ion exchange resin (DOWEX 66 by Dow Chemcial Japan Co.) and 500ml of acetone as a reaction solvent were set in advance in a 1l-capacity glass flask equipped with an agitator, thermometer, and a Dimroth-type cooling tube. 117.6g (0.75 mol) of methyl 2,3-dichloropropionate containing 100ppm of phenothiazine was dropped over a 1-hour period while retaining 25°C and stirring inside the reaction container. After stirring it for 1 more hour at 25°C, the weakly basic ion exchange resin and its salt were separated by means of filtering. After distilling off the acetone inside the filtrate, the filtrate was distilled under a reduced pressure of 30mmHg (abs), and a distillate, which was 78.0g (yield: 86.4%) of methyl 2-chloroacrylate at a boiling

point 46 ~ 47°C, was obtained.

Working Example 2

In the same manner as Working Example 1, 93.9g (0.38 mol) of methyl 2,3-dibromopropionate was dropped over a 1-hour period in the presences of 300ml of a weakly basic ion exchange resin (DOWEX 66) and 350ml of acetone, and after stirring it for 1 more hour at 25°C, the resin was separated by means of filtering. After distilling off the acetone inside the filtrate, the filtrate was distilled under a reduced pressure of 30mmHg (abs), and a distillate, which was 51.6g (yield: 82.3%) of methyl 2-bromoacrylate at a boiling point 62 ~ 63°C, was obtained.

Working Example 3

In the same manner as Working Example 1, 128.3g (0.38 mol) of ethyl 2,3-dichloropropionate was dropped over a 1-hour period in the presences of 500ml of a weakly basic ion exchange resin (DOWEX 66) and 500ml of acetone, and after stirring it for 1 more hour at 30°C, the resin was separated by means of filtering. After distilling off the acetone of the solvent, the filtrate was distilled under a reduced pressure of 25mmHg (abs), and a distillate, which was 89.1g (yield: 88.3%) of ethyl 2-chloroacrylate at a boiling point 52 ~ 53°C, was obtained.

Working Example 4

In the same manner as Working Example 1, 71.6g (0.36 mol) of n-butyl 2,3-dichloropropionate was dropped over a 45-minute period in the presences of 300ml of a weakly basic ion exchange resin (DOWEX 66) and 300ml of acetone, and after stirring it for 1 more hour at 30°C, the resin was separated by means of filtering. After distilling off the acetone

of the solvent, the filtrate was distilled under a reduced pressure of 7 ~ 8mmHg (abs), and a distillate, which was 47.7g (yield: 81.6%) of n-butyl 2-chloroacrylate at a boiling point 60 ~ 61°C, was obtained.

Working Example 5

In the same manner as Working Example 1, 102.0g (0.40 mol) of ethylhexyl 2,3-dichloropropionate was dropped over a 1-hour period /223
in the presences of 300ml of a weakly basic ion exchange resin (DOWEX 66) and 300ml of acetone, and after stirring it for 1.5 more hours at 30°C, the resin was separated by means of filtering. After distilling off the acetone of the solvent, the filtrate was distilled under a reduced pressure of 2mmHg (abs), and a distillate, which was 74.0g (yield: 84.7%) of 2-ethylhexyl 2-chloroacrylate at a boiling point 80 ~ 82°C, was obtained.

Working Example 6

In the same manner as Working Example 1, 22.1g (0.10 mol) of phenyl 2,3-dichloropropionate was dropped over a 30-minute period in the presences of 100ml of a weakly basic ion exchange resin (DOWEX 66) and 150ml of acetone, and after stirring it for 1.5 more hours at 30°C, the resin was separated by means of filtering. After distilling off the acetone of the solvent, the filtrate was distilled under a reduced pressure of 10mmHg (abs), and a distillate, which was 13.0g (yield: 70.2%) of phenyl 2-chloroacrylate at a boiling point 99 ~ 101°C, was obtained.

Working Example 7

In the same manner as Working Example 1, 78.4g (0.50 mol) of methyl 2,3-dichloropropionate was dropped over a 50-minute period in the

presences of 170ml of a weakly basic ion exchange resin (KEX 316 by Koei Chemical Co.) and 300ml of acetone. After the dropping was finished, the solution's temperature was increased to 56 ~ 58°C and stirring was continued for 2 more hours. After cooling it to room temperature, the resin was separated by means of filtering. After distilling off the acetone of the solvent, the filtrate was distilled under a reduced pressure of 33mmHg (abs), and a distillate, which was 49.0g (yield: 81.3%) of methyl 2-chloroacrylate at a boiling point 49 ~ 50°C, was obtained.

Working Example 8

The weakly basic ion exchange resin that was utilized in Working Example 1 and then collected was recycled by means of a 10%-NaOH aqueous solution. By using this, 77.9g (yield: 86.3%) of methyl 2-chloroacrylate was obtained in the same manner as in Working Example 1.

Working Example 9

The weakly basic ion exchange resin that was utilized in Working Example 8 and then collected was recycled by means of a 10%-NaOH aqueous solution. By using this, 78.0g (yield: 86.4%) of methyl 2-chloroacrylate was obtained in the same manner as in Working Example 1.

Comparative Example 1

66.5g of methyl 2,3-dichloropropionate and 200g of a sodium hydroxide aqueous solution were set in a 500ml-capacity glass flask equipped with an agitator, thermometer, and a Dimroth-type cooling tube, and the mixture was heated under reflux for 8 hours. After cooling it to room temperature, the reactant was extracted by means of diethylether. As a result of analyzing the ether layer by means of gas chromatography, the conversion

ratio of the methyl 2,3-dichloropropionate remained at 67.3% and methyl alcohol, which was the hydrolysis product of the methyl ester, was detected.

Comparative Example 2

66.5g of methyl 2,3-dichloropropionate containing 100ppm of phenothiazine and 23.0g of concentrated sulfuric acid were set in a 200ml-capacity glass flask equipped with an agitator, thermometer, and a Dimroth-type cooling tube. The mixture was heated to 100°C while being stirred, and by blowing in dry air into the reaction container at 45ml/minute, the reactant was distilled off for 6 hours. As a result of analyzing the distillate by means of gas chromatography, the yield of methyl 2-chloroacrylate remained at 57.8%, and a polymer had been produced in the reaction container.

Comparative Example 3

150ml of a weakly basic ion exchange resin (DOWEX 66 by Dow Chemcial Japan Co.) and 150ml of isobutyl methyl ketone as a reaction solvent were set in advance in a 300ml-capacity glass flask equipped with an agitator, thermometer, and a Dimroth-type cooling tube, and the interior of the reaction container was heated to 95°C. 31.4g of methyl 2,3-dichloropropionate containing 100ppm of phenothiazine was dropped over a 30-minute period while stirring, and stirring was continued for 1 more hour while maintaining 95°C. After cooling it to room temperature, the resin was separated by means of filtering and methyl 2-chloroacrylate was isolated by means of distillation. The yield remained at 36.3%, and

the ion-exchange capacity of the recycled ion-exchange resin was lower.

Comparative Example 4

Working Example 1 was repeated except for changing the used amount of the weakly basic ion exchange resin to 200ml. After the reaction /224 was finished, an analysis was conducted by means of gas chromatography. As a result, the conversion ratio of methyl 2,3-dichloropropionate remained at 48.1%.

Comparative Example 5

Working Example 1 was repeated except for using a strongly basic ion exchange resin (DOWEX MSA-1). After the reaction was finished, an analysis was conducted by means of gas chromatography. As a result, the conversion ratio of methyl 2,3-dichloropropionate remained at 2.3%, indicating that reactions hardly took place.